Quantification of Aerosol Species with the AMS:

Part I: Overview

AMS Users Meeting, Lund, Sweden
Aug 2019
How do we go from measured MS Ion intensities, to mass concentrations of species?

- Ammonium: 4.8 ug/m³
- Nitrate: 5.8 ug/m³
- Sulphate: 9.4 ug/m³
- Organics: 13.4 ug/m³
- Chloride: 0.15 ug/m³

*Mexico City 2/2002*
AMS Mass Quantification

Converting AMS ion signal to species mass concentrations

\[
\text{mass}_{\text{species}} \propto \frac{1}{IE_{NO3}} \cdot \frac{1}{RIE_{\text{species}}} \cdot \frac{1}{CE} \cdot \frac{1}{Q} \sum_{\text{all } i} I_{s,i}
\]

- Ionization Efficiency \((IE_{NO3})\)
- Flow \((Q)\)
- Collection Efficiency \((CE)\)
- Relative Ionization Efficiency \((RIE_s)\)
Collection Efficiency

Efficiency with which particles are transmitted to and collected at vaporizer

\[ CE(d_{va}) = E_L(d_{va}) \times E_s(d_{va}) \times E_b(d_{va}) \]

Lens Transmission

Overlap between particle beam and vaporizer

Particle Bounce on oven
Collection Efficiency: EL

Standard Lens: Liu et al. (2007)

![Graph showing Collection Efficiency (EL) as a function of vacuum aerodynamic diameter (d_va) for different torr pressures. The graph compares experimental data with CFD model predictions.]

PM2.5 Lens: Liu et al. (2017)

AMS, ACSM, SP-AMS: All use same Lens, same CE_L effects

E_L: Size dependent Transmission through lens
Collection Efficiency: \( Es \)

Most particles (even aspherical soot particles) are collected with greater than 95% efficiency.

\( Es \approx 1 \) (AMS and ACSM Thermal Vaporizers)

Some irregular particles may miss vaporizer.
Collection Efficiency: $E_s$<1 (SP - AMS Laser Vaporizer)
Collection Efficiency: Eb

AMS and ACSM: SV Thermal Vaporizer
- Bounce Loss is dominant
  \[ Eb < EL < Es \]
- \( f(\text{composition, phase, particle size}) \)

AMS and ACSM: CV Thermal Vaporizer
\[ Eb = 1 \]

SP-AMS: SP-mode (Laser Vaporizer)
No Bounce

Eb: Correction factor for particle bounce off Vaporizer

SV: Flash Vap

SV: Bounce

CV: Capture

Xu et al., 2017
**CE: Lab and Field Results**

$E_b$ is dominant contribution to CE and affected by particle bounce (depends on particle phase)

- **Eb affected by**
  1. nitrate content
  2. acidity/neutralization
  3. Relative humidity in the sampling line
  4. organic liquid content

Standard Vaporizer

References: Matthews et al., Quinn et al., Allan et al., Drewnick et al.

Typically, ambient CE=0.5 (+/-0.15) for all species with empirical composition dependence (Middlebrook et al.)

Lab CE$_S$ values are more variable since pure particles may not be identical in phase to complex, ambient particles (Matthews et al., Docherty et al.)
Composition Dependent CE (CDCE) is incorporated into Squirrel/PIKA for ambient applications.
AMS Mass Quantification

Converting AMS ion signal to species mass concentrations

$$mass_{species} \propto \frac{1}{IE_{NO3}} \cdot \frac{1}{RIE_{species}} \cdot \frac{1}{CE} \cdot \frac{1}{Q} \sum_{all\ i} I_{s,i}$$

Ionization Efficiency ($IE_{NO3}$)
Flow (Q)
Collection Efficiency (CE)
Relative Ionization Efficiency ($RIE_s$)
RIE (Relative Ionization Efficiency)

Inorganic Species
Early lab calibrations on inorganics by Frank Drewnick, Ann Middlebrook

$\text{RIE}_{\text{NO}_3} = 1.1$ (for ions other than $m/z$ 30 and 46)
$\text{RIE}_{\text{NH}_4} = 3-5$
$\text{RIE}_{\text{SO}_4} = 1.2$

$\text{IE}_{\text{NO}_3}$, $\text{RIE}_{\text{NH}_4}$, are routinely calibrated for each instrument
$\text{RIE}_{\text{SO}_4}$ can be measured for each instrument.
Determination of RIE for Organics

Complication: Ambient OA is made up of thousands of individual organic species. What do we use as a calibrant?

Laboratory Measurements:
- For laboratory SOA, CE is widely variable
- Mass concentrations should be measured w/ SMPS as well

Ambient Measurements:
Usually $CE \times RIE_{\text{Org}} = (0.5 \times 1.4) = 0.7$
- $CE=0.5$ assumes organic and inorganics internally mixed
- $RIE_{\text{Org}} = 1.4$ is based on laboratory work by Silva et al. (2001)
**Improved Calibration Protocol for RIE_{OA}**

*Xu et al. AS&T,(2018)*

**Data Processing**

- Input Mass = (CPMA Mass/particle)\*CPC Number
- AMS Mass = (1/CES\*RIE_{S})\*AMS NO3 Equiv. Mass

**CE_{S}*RIE_{S} = NO_{3} Equiv. Mass/CPMA Input Mass**

**CE_{S} ~ AMS pTOF Single Particle Counts/ CPC OR AMS LS Particle Counts/ CPC**

**Measurements**

- Number Conc (CPC)
- Mass Conc Q-AMS\(^\ast\) (w/ LS) with standard vaporizer and Capture Vaporizer (CE~1)
Measurements of Commercially available Organic Standards, PAM SOA
Lab $\text{RIE}_{\text{OA}} = 1.7$ for $\text{Osc} > -1.5$ (within 20% uncertainty of 1.4 used for ambient
Could RIE of ambient POA and SOA be different?

**RIE$_{OA}$ vs OSC**

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Xu et al.
AS&T,(2018)
Online Chemical Characterization of Food-Cooking Organic Aerosols: Implications for Source Apportionment

Ernesto Reyes-Villegas, Thomas Bannan, Michael Le Breton, Archit Mehra, Michael Priestley, Carl Percival, Hugh Coe, and James D. Allan

Measured $RIE_{COA}$ is 1.56-3.06

Agrees with expected RIE range for Xu et al. AS&T,(2017)
Ambient OA trends do not show evidence for large differences in $RIE_{POA}$ and $RIE_{SOA}$

Trends in SOA and POA RIE may be offset by their differences in $CE_L$ (POA sizes fall in small size range (<100 nm) where lens cutoff can be significant)

- Need for more of these careful intercomparisons in high POA environments
Simpler RIE\textsubscript{OA} Calibrations

Can we obtain RIEs of organics by mixing with NH\textsubscript{4}NO\textsubscript{3} and directly measuring org/NO\textsubscript{3} ratio compared to known value from DMA&CPMA size and mass selection?

*Works for mixed inorganic particles*

Advantage:
Direct ratio to NO\textsubscript{3} for internally mixed particles offsets need to measure CE\textsubscript{B} which is variable for lab particles.

*Xu et al.*
*AS&T, (2018)*
Lab: Binary Organic/NO₃ Particles

WORKS WELL for Mixed Alcohol particles
- $\text{RIE}_{\text{Org}}$ and $\text{RIE}_{\text{NH}_4}$ agree well with measurements from pure particles

DOES NOT WORK for Mixed Acid particles
- $\text{RIE}_{\text{Org}}$ and $\text{RIE}_{\text{NH}_4}$ higher than measurements from pure particles

- Mixed Acid and nitrate particles may lose NO₃ through displacement reaction and volatilization of HNO₃
- Mixed particles (nitrate + alcohol (sucrose, xylitol, levoglucosan)) provide an easier method of calibrating reference $\text{RIE}_{\text{Org}}$ values

Xu et al. AS&T, (2018)